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Studies on the Active Carbon.

IV. The Electrical Resistance of the Active Carbon (2)

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I. Introduction.

The electrical resistance of amorphous carbon was studied for the purpose of the determination of the quality of the carbon electrode or the powdered carbon for the receiver of the telephone.¹⁾²⁾

Recently the determination of the electrical conductivity of the active carbon is considered to be very important not only for the qualification of the air cell electrode, but for also the activity of the active carbon, which is thought to have some relation to the electrical conductivity.³⁾

2. Experiment.

a) Sample

1) The active carbons produced from "Hinoki" (*Chamaecyparis obtusa* S. et Z.), "Akamatsu" (*Pinus densiflora* S. et Z.), "Sugi" (*Cryptomeria japonica* D. Don.), "Kusunoki" (*Cinnamomum camphora* Sied.), "Kaba" (*Betula nikoensis* Koiz.), "Yukarinoki" (*Eucalyptus globulus* Labill.), "Kiri" (*Paulownia tomentosa* Stead), "Yachidamo" (*Fraxinus Mandshurica* Rhr.), and lignin according to borax-boric acid preparing method.⁴⁾

2) The commercial active carbons were prepared by Takeda Pharmaceutical Industries, Ltd., Shikoku-kagaku Co., Shimonozato-seiyaku Co., Tokyo-oka Co., Futamura-kagaku Co., Tokyo-gasu Co., and Taihei-sangyo Co.

The hard granular active carbon "Tokyo-gas" and ground active carbon "Taihei" were ground in a ball mill.

3) The active carbon produced from "Akamatsu" and lignin by the zinc chloride method.

b) Apparatus and Measuring procedure

The measuring apparatus and procedure have been described in the previous report.⁴⁾ The iron piston is put in the ebonite cylinder from upside. Silver plates are fixed to the end of the iron piston and to that of the iron plate and

are used for the electrodes. The electrical resistance is measured by the Wheatstone bridge method. The resistance of the powdered carbon is to change with the applied pressure, while the resistance of the powdered carbon has hitherto been measured under the pressure 200–300 kg/cm². But in this experiment the resistance is measured in the free heaped state, because this resistance also will show one of the electrical properties of the active carbon.^{5) 6)}

It is found that the electrical resistance of the active carbon produced from "Hinoki", "Akamatsu", "Sugi", "Kusunoki", "Yukari", "Kiri", "Kaba", "Yachidamo", and lignin is 10¹–10² Ω/cm³, according to the borax-boric acid preparing method.

Table 1 Electrical Resistance of Active Carbon
(Borax-Boric acid Method. Max. Temp. 850°C)

	Electrical Resistance. Ω/cm ³	Surface Area m ² /g	Ash %	Specific Vol. cc./g
Hinoki	2.76×10 ²	133	1.26	3.1
Matsu	8.80×10 ²	60	0.12	3.5
Sugi	1.25×10 ²	98	1.27	3.6
Kusunoki	4.50×10 ¹	84	0.19	3.2
Yukari	2.30×10 ¹	108	1.25	3.6
Kaba	1.10×10 ²	60	2.36	2.7
Yachidamo	1.0 ×10 ²	78	3.09	3.3
Kiri	1.10×10 ²	60	1.37	3.5
Mitsumata	1.60×10 ²	130	2.40	3.8
Lignin	5.90×10 ¹	260		2.6

The specific resistance of the wood charcoal is 10⁵–10⁶Ω/cm³ and that of the graphite is 10¹–10²Ω/cm³.^{7) 8)}

The active carbon is considered as the partial graphitizing product of the charcoal. When the activating temperature is increased, or the charcoal is activated at higher temperature, the specific resistance of the produced activated carbon is supposed to be lower.⁸⁾

Table 2

	Maximum Temperature				
	Unteated	650°C	750°C	850°C	950°C
Yield %	...	22.0	17.0	16.6	8.5
Electrical resistance	1.0×10 ⁵	1.0×10 ⁵	1.0×10 ⁵	1.0×10 ²	1.0×10 ¹
Surface area m ² /g	78	84
Specific volume cc/g	...	3.4	3.1	2.9	3.1
Ash %	2.45	2.75	4.73	1.75	1.26

"Hinoki" was activated by the borax-boric acid method at 650°, 750°, 850° and 950°C. The properties of these activated carbons are shown in table 2.

In this case, the surface area of the activated carbon is 78m²/g—according to Paneth 1 mg of methylene blue in a monomolecular layer covers 1 m²/g active carbon⁹⁾—and the specific resistance of it is 10²Ω/cm³ at 850°C. In proportion that the activation temperature becomes higher, the resistance of the activated carbon becomes lower.

The properties of the commercial active carbon are examined and are shown in table 3.

Table 3 Properties of the Commercial Active Carbons

	Electrical resistance Ω/cm ³	Surface area m ² /g	Adsorp. power caramel %	Ash %	Colour of Ash	Specific volume cc./g
Takeda	1.0 × 10 ⁵	212	73.8	4.19	reddish brown	3.7
Shikoku	1.0 × 10 ⁴	108	61.6	3.99	white	2.6
Shimozato	1.0 × 10 ⁴	162	56.3	7.81	gray	2.2
Tokyo-oka	1.0 × 10 ⁰	198	58.0 ^{a)}	1.81	gray	2.2
Futamura	1.0 × 10 ⁵	150	80.2 ^{a)}	5.96	reddish brown	3.6
Tokyo-gas ^{a)}	1.0 × 10 ⁰	174	64.5 ^{a)}	5.21	dark gray	3.5
Taihei ^{c)}	1.0 × 10 ⁵	60	23.0 ^{a)}	80.4	white	1.2

a) Raw sugar solution 15° Brix

b) Hard granular active carbon was ground in a ball mill

c) Crushed type active carbon was ground in a ball mill

The surface area of the commercial carbons—calculated from the methylene blue method⁹⁾—is 212–108 m²/g ("Taihei" was omitted in this discussion because its ash content was too high and the adsorptive power of it was very poor,) and the in electrical resistance is 10⁰–10⁵Ω/cm³, but that of "Takeda" and "Futamura" is 10⁵Ω/cm³.

The colour of the ash of these two active carbons is reddish brown and the decolourizing power of caramel or that of raw sugar solution is more excellent than others. So these two active carbons are supposed that they should be prepared by the zinc chloride method.

Table 4

	Electrical resistance Ω/cm ³	Surface area m ² /g	Adsorptive power raw sugar %
Akamatsu	3.4 × 10 ³	215	78.0
Hinoki	7.5 × 10 ³	238	82.2
Lingnin	1.4 × 10 ⁴	240	56.0

The resistance of the active carbon made from "Akamatsu" and lignin which were prepared by the previous zinc chloride process¹⁰⁾ is shown in table 4

The resistance of the active carbon prepared by the zinc chloride method was found as high as that of wood charcoal.

When the active carbons—"Takeda", "Futamura", "Akamatsu", and lignin were heated at 850°C. by the the same method as the reactivation, the resistance of them is found reduced to 10^1 – $10^0 \Omega/\text{cm}^3$.

Table 5

	Resistance Ω/cm^3	Surface area m^2/g	Adsorptive power raw sugar %
Takeda	3.0×10^0	240	93.5
Futamura	6.0×10^0	156	91.8
Akamatsu	3.0×10^1	228	81.3
Lignin	5.0×10^0	254	60.6

The active carbons of "Takeda" and "Akamatsu" were heated at 500°, 600°, 700°, 800° and 900°C. in a electrical furnace. Their resistance decreased with the increase of temperature, but, the surface aera and the active power of them remained almost unchanged.

Table 6

Max. heating temp. °C	Akamatsu			Takeda		
	Electrical resistance Ω/cm^3	Surface area m^2/g	adsorp. power raw sugar %	Electrical resistance Ω/cm^3	Surface area m^2/g	Adsorption power raw Sugar %
...	3.4×10^3	180	78.0	1.0×10^5	225	78.8
500	6.6×10^3	234	91.8
600	6.6×10^2	216	8.0	4.6×10^3	246	92.6
700	1.5×10^2	246	81.5	4.0×10^3	246	92.5
800	1.5×10^2	240	93.5
900	6.4×10^0	240	82.2	1.5×10^0	240	95.5

Their maximum surface area, calculated by methylene blue method, was at 750°C, and decolorization power of the caramel or raw sugar solution showed gradual increase.

The resistance of the zinc chloride activated carbon is decreased by heating it up to 500°–850°C. One of the reasons for the high resistance is supposed to be due to the length of the hour between the time of manufacture and test.

The carbon of "Takeda", which has been heated at 850°C. was placed in

open air, in a desiccator, or in a crucible placed in a weighing bottle which contained water or benzene.

These experimental result is shown table 11.

Table 7

	In Open air	In desicator	In a weighing bottle		
			Water	Benzen	Benzen*
Adsorped %			97.5	118	111
Resistance Ω/cm^3	5.0×10^2	7.0×10^1	5.0×10^1	5.0×10^1	5.0×10^1

* Untreated active carbon.

The resistance of the active carbon which is placed in the open air was higher than that of in the desicator, but the resistance in other cases does not change in the experiments of the succeeding three monthes.

What occurs during activation is not clarified at present, but it is evident the activated carbon increases in the surface area and turns to a very porous structure. The active center of the carbon are on the surface of the carbon particles.

In the activation of the charcoal it is considered that the hydrocarbons which deposited on the surface on the charcol during the 1st step of arbonization could be removed by heating at 650°C. or higher, and then clear carbon surface appears.

The activation in the zinc chloride method proceed as follows; the concentrated zinc chloride solution which contains 0.5 to 4.0 parts of zinc chloride is mixed with one part of the saw dust,—in some cases, hydrochloric acid or phosphoric acid is added—and after drying, the mixture is heated in a kiln at 400°–900°C. until zinc chloride vapour comes forth in copious quantity, and thus the porosity of the carbon increases and the pore size is enlarged more than that of the steam activated carbon.

This is the reason why the zinc chloride activated carbon is more fitted as decolourizing active carbon for the refinement of the raw sugar which contains larger colouring particles.

If these pores are filled up with air which is the electrically non-conducting gas, the free heaped contact electrical resistance must be increased.

This would be one of the reasons why zinc chloride activated cabon shows the high resistance while the surface area and the decolourizing power of caramel or the raw sugar are very excellent.

3. Résumé

1) It is found that the electro-resistance of the active carbon produced from "Hinoki", "Akamatsu", "Sugi", "Kusunoki", "Yukari", "Kiri", "Yachidamo", and lignin according to the borax-boric acid method is 10^1 - $10^2 \Omega/\text{cm}^3$, and that the activation temperature becomes higher, with the resistance becoming lower.

2) The resistance of the commercial active carbons is 10^2 - $10^4 \Omega/\text{cm}^3$ but that of "Takeda" and "Futamura" is $10^5 \Omega/\text{cm}^3$. The electro-resistance of the active carbon prepared by the zinc chloride method is found as high as that of charcoal.

3) The active carbon of "Takeda" and "Akamatsu" which has been prepared by the zinc chloride method is heated 500°C . or higher. The resistance of them changed lower with increase of temperature, but the surface area and the active power of them remains almost unchanged.

4) One of the reasons for the high electro-resistance is supposed to be due to long period between the time of manufacture and test. The activated carbon, "Takeda", which have been heated at 850°C . was placed in open air, and in a desiccator. The electro-resistance of the former is higher than that of the latter slightly, in the experiments of the succeeding three months.

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